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In this paper, time-dependent density functional theory (TDDFT) calculations of excited state polarizabilities of conjugated molecules are presented. The increase in polarizability upon excitation was obtained by evaluating the dependence of the excitation energy on an applied static electric field. The excitation energy was found to vary quadratically with the field strength. The excess polarizabilities obtained for singlet excited states are in reasonable agreement with the experimental results for the shorter oligomers, particularly if the experimental uncertainties are considered. For longer oligomers the excess polarizability is considerably overestimated, similar to DFT calculations of ground state polarizabilities. Excess polarizabilities of triplet states were found to be smaller than those for the corresponding singlet state, which agrees with experimental results that are available for triplet polarizabilities. Negative polarizabilities are obtained for the lowest singlet A_g states of longer oligomers. The polarizability of the lowest B_u and A_g excited states of the conjugated molecules studied here are determined mainly by the interaction between these two states. Upon application of a static electric field a quadratic Stark effect is observed in which the lower B_u state has a positive excess polarizability and the upper A_g state exhibits a decrease in polarizability upon excitation. All results are explained in terms of a sum-over-states description for the polarizability. [DOI: 10.1063/1.1415085]

INTRODUCTION

The electrostatic properties of molecules in their electronically excited states are of considerable interest since they determine many of their observable properties and they contain information on the nature of excited states. Upon excitation both dipole moment and polarizability of a molecule can change. These changes can for instance result in a large effect of an environment, e.g., a solvent shell, on the absorption spectrum.[1] Changes in dipole moment alter the electrostatic interaction with the solvent in the ground and excited state, which causes a shift in the absorption maximum. These effects are used in solvent polarity scales such as the well-known ET_{30} scale.[2] A less recognized environment effect is caused by changes in polarizability, which causes a change in the dispersion (van der Waals attraction) interaction between a molecule and its surroundings.[1,3] A striking example of environment effects on electronic spectra is found in the biologically important retinal where the absorption maximum shifts from 450 nm in solution to 568 nm when it is embedded in bacteriorhodopsin.[4]

Changes in polarizability upon excitation also contain valuable information on the nature of molecules in their electronically excited state, the so-called exciton state.[5–7] This is of particular interest in the research of π-conjugated polymers and oligomers. These materials are intensively studied at present because of their semiconducting and light-emitting properties which make them attractive candidates for application in polymer or molecular electronic devices such as light emitting diodes (LEDs) and field effect transistors (FETs). The increase in polarizability upon excitation (excess polarizability $\Delta\alpha$) can be considered as a measure for the spatial extent of the exciton. The lowest singlet exciton is the intermediary state in organic LEDs[8] and photovoltaic devices.[9,10]

Finally, the electrostatic properties of excited states are important for studying materials, which exhibit nonlinear optical (NLO) behavior.[11] In the two-state model the first hyperpolarizability is proportional to the change in dipole moment upon excitation, $\Delta\mu$. In solution, $\Delta\mu$ is affected also by the change in polarizability since the electric field of the surrounding solvent induces a dipole moment of a different size.

For the experimental determination of excited state electrostatic properties there are mainly two techniques available. The first is the Stark spectroscopy or electroabsorption/emission method.[12] In this method the effect of a strong external electric field on the absorption or emission spectrum is evaluated. The effect of the electric field is observed as a broadening of the absorption band if there is a change in the dipole moment upon excitation, which is a result of the random orientation of molecules with respect to the applied field. A change in polarizability causes a shift of the absorption/emission band, which is quadratically dependent on the applied field. The method can be used either in absorption or emission spectroscopy. In the case of electroabsorption, information is obtained on the properties of the Franck–Condon excited state whereas in electroemission this information is obtained for the relaxed excited state. This method has often been applied in studies of chromophores in biologically important systems[13–16] but also in the study of donor–acceptor molecules for NLO applications.[11,17]

The second method by which information on the excited state electrostatic properties can be obtained is the flash photolysis time-resolved microwave-conductivity (FP–TRMC) technique.[5,7,18–20] In this technique the changes in molecular properties upon excitation with a short nanosecond laser pulse are probed using microwaves. A change in dipole moment results in absorption of microwaves while a change in the polarizability (which changes the dielectric constant of the sample) causes a phase shift of the microwaves. The information obtained in this way usually corresponds to the relaxed excited state, generally the lowest singlet state. In materials with an appreciable singlet–triplet transition probability such as oligothiophenes also the properties of the lowest triplet state can be obtained.[21]

While there is a large amount of experimental data available on excited state properties there have been very few theoretical studies, especially for the calculation of excess polarizabilities. This is not very surprising since experimental studies very often involve large molecules not accessible to accurate *ab initio* methods taking electron correlation in consideration, such as configuration interaction including single and double excitations (CISD) or complete active space multiconfiguration self-consistent-field (CASSCF) methods combined with large basis sets. This restricts the applicability of these methods to rather small molecules such as benzene and polyenes.[22,23] Semiempirical methods have also been used for calculating excited state polarizabilities. Such methods have been applied with reasonable success for the calculation of excess polarizabilities in biphenyl polyenes, however, considerable deviations from experimental results were observed in the case of donor–acceptor substituted polyenes.[13,24]

Recently, Van der Horst *et al.*[25] have calculated polarizabilities of exciton states of conjugated polymers by applying the Bethe–Salpeter equation (BSE) for the description of an electron–hole pair. The results obtained from these calculations were in reasonable agreement with experimental data, however they were performed for infinitely long and periodic polymer chains. This is a rather crude approximation since conjugated polymers in solution in general have a disordered structure.

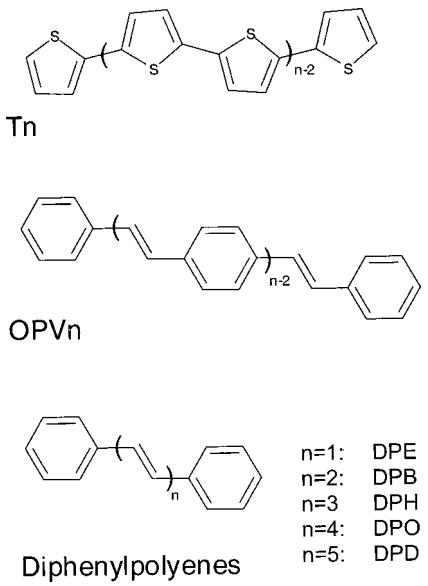

FIG. 1. Molecular structure and nomenclature for molecules studied in this work, note that OPV2 is the same as DPE.

Density functional theory (DFT) offers a very attractive alternative to the traditional correlated *ab initio* methods since it can treat very large systems at the correlated level at a computational cost comparable to that for Hartree–Fock calculations. DFT is in principle a ground state theory, however the recent implementations of time-dependent density functional theory (TDDFT)[26] have made the evaluation of excitation spectra possible and it has been shown that reliable results can be obtained from this method.

In this paper we demonstrate the use of time-dependent density functional theory combined with a static electric field for the calculation of the change in polarizability upon excitation, $\Delta\alpha$, for conjugated oligomers of three different types: oligothiophenes, oligophenylenevinylenes, and diphenylpolyenes. The molecular structures of these oligomers are shown in Fig. 1, together with the nomenclature used in this paper. Calculations are performed for molecules in vacuum and the results are compared to experimental data from both Stark spectroscopy and FP–TRMC for isolated molecules in solution.

THEORY AND COMPUTATIONAL DETAILS

All the calculations described below were performed using the time-dependent density functional theory code as implemented in the Amsterdam Density Functional Program Package (ADF).[27–30]

For the ground state calculations the local density approximation (LDA) for the exchange and correlation functional based on the parametrization of the electron gas data given by Vosko, Wilk, and Nusair (VWN)[31] was used, together with the generalized gradient approximation corrections by Becke[32] (exchange) and Perdew[33] (correlation).

The basis set used for the calculations below was of triple zeta quality including polarization functions (TZP, ba-

sis set IV in ADF) consisting of Slater-type functions. Polarizabilities of these systems were calculated using response theory based on time-dependent density functional theory (TDDFT) as implemented in the RESPONSE code of ADF,[26,30,34] in combination with a static electric field (see below).

TDDFT provides a method for calculating frequency-dependent (and static) polarizabilities, excitation energies and several other response properties. The calculation of excitation energies and oscillator strengths goes practically through the solution of the following eigenvalue equation:[26]

$$\Omega \mathbf{F}_i = \omega_i^2 \mathbf{F}_i , \tag{1}$$

where the four-index matrix Ω has components given by

$$\Omega_{ia\sigma,jb\tau} = \delta_{\sigma\tau}\delta_{ij}\delta_{ab}(\varepsilon_{a\sigma}-\varepsilon_{i\sigma})^2 + 2\sqrt{(\varepsilon_{a\sigma}-\varepsilon_{i\sigma})}K_{ia\sigma,jb\tau}\sqrt{(\varepsilon_{b\tau}-\varepsilon_{j\tau})}. \tag{2}$$

In this equation the squared differences between occupied and virtual KS orbital energies (a,b refer to unoccupied and i,j refer to occupied ones, while σ and τ are spin indices) are included as well as a coupling matrix, K containing Coulomb and exchange correlation (XC) parts. The square of the desired excitation energies are the eigenvalues ω_i^2, while the oscillator strengths are simply related to the eigenvectors F_i. The elements of the eigenvectors F_i are roughly comparable to the CI coefficients in a singly excited configuration interaction (SECI) calculation and are a measure to what extent the corresponding excitation can be interpreted as a pure single particle excitation or if several such excitations play a crucial role in the transition. The Coulomb part of the coupling matrix is given by

$$K^{\mathrm{Coul}}_{ij\sigma,kl\tau} = \int d\mathbf{r} \int d\mathbf{r}' \; \phi_{i\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi_{k\tau}(\mathbf{r}')\phi_{l\tau}(\mathbf{r}'). \tag{3}$$

While the exchange correlation part

$$K^{\mathrm{xc}}_{ij\sigma,kl\tau}(\omega) = \int d\mathbf{r} \int d\mathbf{r}' \; \phi_{i\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r}) f^{\sigma\tau}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',\omega)\phi_{k\tau}(\mathbf{r}')\phi_{l\tau}(\mathbf{r}') \tag{4}$$

is related to the so-called exchange correlation kernel

$$f^{\sigma\tau}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',t-t') = \frac{\delta \nu^{\sigma}_{\mathrm{xc}}(\mathbf{r},t)}{\delta \rho_{\tau}(\mathbf{r}',t')}. \tag{5}$$

In the so-called adiabatic local density approximation (ALDA) used here the exchange correlation kernel is simply given by

$$f^{\mathrm{ALDA},\sigma\tau}_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',\omega) = \delta(\mathbf{r}-\mathbf{r}') \left. \frac{\delta \nu^{\mathrm{LDA},\sigma}_{\mathrm{xc}}(\mathbf{r},t)}{\delta \rho_{\tau}} \right|_{\rho_{\tau}=\rho_{0,\tau}(\mathbf{r})}. \tag{6}$$

The matrix Ω can become rather large, however, since one is usually interested in the lowest few excitations, efficient algorithms such as the Davidson algorithm can be used.[35–37] The TDDFT method as implemented in ADF can be used to calculate accurate excitation energies and has been successfully applied to the excited states of oligothiophenes.[38]

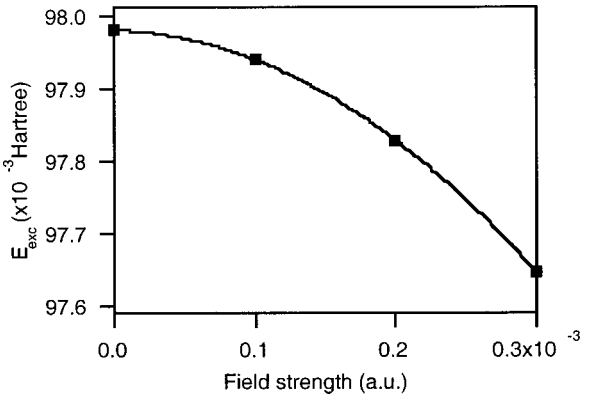

FIG. 2. Excitation energy plotted vs electric field strength for lowest singlet excitation in OPV3. The squares represent calculated values, the line is a parabolic fit.

The combination of TDDFT with a static uniform electric field makes possible to analyze the electrostatic properties of molecules in their excited state. The dependence of the excitation energy on a static external electric field depends on the changes in dipole moment and polarizability upon excitation. A change in dipole moment gives a linear dependence on the applied electric field whereas a change in polarizability causes a quadratic field dependence of the excitation energy:

$$E_{\mathrm{exc}}(F) = E_{\mathrm{exc}}(0) - \Delta\mu F - \tfrac{1}{2}\Delta\alpha F^2, \tag{7}$$

where F is the static electric field. This method for the calculation of the changes in electrostatic properties is in fact analogous to the way in which excited state properties are obtained in electroabsorption measurements. The advantage of calculations is however that there is full control of the orientation of the system that is studied and therefore a change in dipole moment will also cause a shift of the excitation energy as opposed to a broadening of the spectrum which is obtained experimentally because of the random orientation of molecules in the solution or matrix. The molecules that are considered in this work exhibit only an increase in polarizability upon excitation. Hence, the excitation energy varies quadratically with increasing field strength as a results of the quadratic Stark effect. Such a quadratic dependence is demonstrated by the TDDFT calculations as shown in Fig. 2 for OPV3 (see Fig. 1 for nomenclature). Excess polarizabilities reported below were obtained by calculating the excitation energy at zero field and at three different field strengths ranging from 5×10^7 V/m(1×10^{-4} a.u.) to 1.5×10^8 V/m(3×10^{-4} a.u.) and fitting of a parabolic function to the results. The only significant contribution to the excess polarizability was found to be in the direction along the long axis of the molecules studied. The values given below are average values for the increase in polarizability, i.e., averaged over all three directions. The change in dipole moment ($\Delta\mu$) was found to be zero for all studied molecules, as expected. The dependence of the results on the size of the basis set used is shown in Table I for OPV2 (or DPE). Sizes of the basis set range from a minimal basis set (SZ, basis I in ADF)) to triple zeta plus polarization functions (TZP, IV in ADF). All basis sets consist of Slater-type functions. The

TABLE I. Basis set dependence of the excitation energy and excess polarizability for the lowest B_u state of OPV2. ADF basis set names are given in parentheses in the first column.

Basis set	E_{exc} (eV)	$\Delta\alpha$ (Å^3)
SZ (I)	4.46	64
DZ (II)	3.81	46
DZP (III)	3.68	44
TZP (IV)	3.61	47
Experimental	3.71	

calculated excitation energy decreases with increasing size of the basis set, however the calculated excess polarizability does not seem to depend much on the size of the basis set, except for the smallest basis where the polarizability is considerably larger. The differences in $\Delta\alpha$ obtained using the other basis sets are very small and are probably due to numerical imprecision in the Davidson algorithm and in the fitting of the results to parabolic functions. The basis set used for the calculations reported below (TZP, IV) can be considered sufficient for accurate results.

RESULTS AND DISCUSSION

Singlet B_u excitons

The method described in the preceding section was used to calculate excess polarizabilities for three series of π-conjugated oligomers that are of interest for application in plastic electronic devices (see Fig. 1).

The excess polarizabilities calculated for the lowest singlet excitons (of B_u symmetry) of the molecules in Fig. 1 are listed in Table II together with the experimental data collected from both Stark spectroscopy[39,40] and FP–TRMC measurements.[5,19,21] The calculated results for shorter oligomers are shown to be in reasonable agreement with experimental data, especially when the experimental error margins

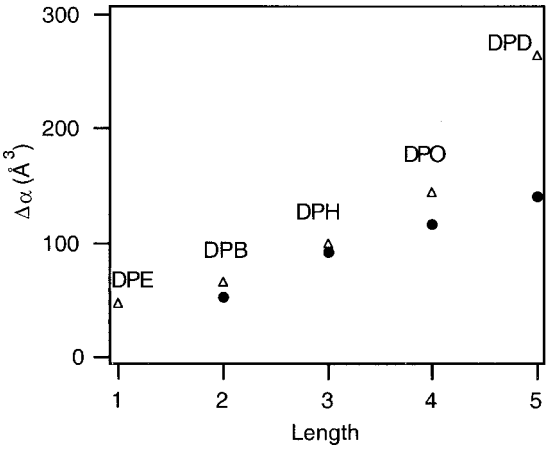

FIG. 3. Trend in excess polarizability of the diphenylpolyenes for the lowest singlet excited state. Triangles are calculated values, circles are experimental values from electroabsorption measurements.

are considered. For longer oligomers (T6, OPV4, and DPD) the polarizability is considerably overestimated in these calculations. This is shown graphically in Fig. 3 for the series of biphenyl polyenes. The calculated results correspond reasonably to the Stark spectroscopy values up to DPO. The calculated $\Delta\alpha$ for DPD deviates considerably from the experimental value. This overestimate for long conjugated system has also been found for ground state polarizabilities of polyenes as reported by Champagne *et al.*[41] This incorrect behavior for long (conjugated) molecules is related to the shortsightedness of present XC potentials which mainly feel the local density and are relatively insensitive to polarization charges induced by an external electric field at the chain ends.[41]

For short oligomers this problem does not arise. For OPV3 the calculated excess polarizability (351 Å^3) is in reasonable agreement with the Stark value (420 Å^3)[40] as well as

TABLE II. Excess polarizabilities for different singlet and triplet excited states (in Å^3) compared to experimental data, where available.

Compound	$\Delta\alpha\,{}^1B_u$ (Calc.)	$\Delta\alpha\,{}^1B_u$ (Expt.)	$\Delta\alpha({}^3B_u)$ (Calc.)	$\Delta\alpha({}^3B_u)$ (Expt.)	$\Delta\alpha({}^1A_g)$ (Calc.)	$\Delta\alpha({}^3A_g)$ (Calc.)
T2	11	125±100[a]	3	4.5[e]	24	34
T3	84	370±100[a]	16	11[e]	−20	12
T4	189	400±100[a]	47	19[e]	−356	24
T5	567	355±50[a]	103	23[e]	−425	51
T6	1429	370±50[a]	198	23[e]	−1183	84
OPV2	47		<10		66	59
OPV3	351	300±50,[b] 420[c]	63		−273	20
OPV4	1283	530±50[b]	205		−1023	89
DPE	47		<10		66	59
DPB	65	53[d]	14		78	43
DPH	100	91[d]	17		−61	20
DPO	145	116[d]	21		−104	24
DPD	265	140[d]	26		−199	25

[a]FPTRMC, Ref. 19.
[b]FPTRMC, Ref. 5.
[c]Electroabsorption, Ref. 40.
[d]Electroabsorption, Ref. 39.
[e]Reference 21.

with the FP–TRMC result (300 ± 50 Å^3),[5] this shows that for shorter oligomers the results are reliable. OPV3 is the only oligomer on which both experimental techniques have been applied and the difference can be interpreted as a rough estimate of the experimental errors, although the difference may also arise because of fundamental differences between both techniques. In FP–TRMC the excess polarizability is measured as the difference between the ground state polarizability in the ground state geometry and the exciton state in its relaxed excited state geometry, whereas in Stark spectroscopy the unrelaxed, initially excited state is probed.

Oligothiophenes and oligophenylenevinylenes can be expected to have different excited state properties than diphenylpolyenes. The diphenylpolyenes are phenyl-endcapped polyacetylenes in which there exist bound exciton states just below the conduction band edge. According to the work of Shibahara *et al.* these excitons have binding energies around 0.2 eV[42] and theoretical studies have shown that they are delocalized over a long distance.[43] A low exciton binding energy for polyacetylene would explain the trend in the experimental values of the excited state polarizabilities very well. In this case, for polyacetylenes the relevant excitonic states are delocalized, and a linear increase in the excited state polarizabilities with the size of the system can be expected, which is indeed observed for the shorter polyenes presented here. The upper limit of the polarizability is probably determined by the degree of structural disorder in these systems. The TDDFT calculations give reasonable numerical agreement with experimental results. One indeed observes a linear increase of the polarizability up to DPO, for longer chains TDDFT overestimates the excited state polarizabilities. This discrepancy is inherent to the theoretical method used and can be attributed to the local character of the XC potentials currently used, as it was explained before.

For the oligothiophenes the situation is somewhat different. Much higher exciton binding energies (0.5–1.0 eV) have been reported in this case. This would lead to the formation of a Frenkel-type exciton which is localized over a much smaller length than the exciton in polyacetylene. The experimental excess polarizability seems to saturate already for T3 which would agree with these arguments. It should be noted however, that the experimental data for the thiophenes are not reliable enough (because of a large uncertainty in the excited state lifetime[19]) to draw definite conclusions in this respect. The TDDFT values are in reasonable agreement for the small oligomers up to T3, there is a large discrepancy with experiment for the larger ones. Oligothiophenes can in general be described as long one-dimensional chains of weakly interacting monomer units. It should be clear that the diphenylpolyenes have a different character because of their low exciton binding energy and may in fact be considered as simple conjugated entities. For the OPVs the same behavior as for the oligothiophenes may be expected, although the excitonic states have a smaller binding energy and the localization length of the exciton is somewhat larger. Here again up to OPV3 there is good agreement between experiment and theory.

Differences in experimental and calculated values for the OPVs and oligothiophenes may be caused by the effect of substituents on the excess polarizability. The calculations all refer to unsubstituted oligomers whereas most of the experimentally studied compounds have substituents. In the case of the OPVs this effect is probably not very large since the substituents in this case are *t*-butyl groups at the two outermost rings of the molecule.[5] These alkyl side chains are not expected to have a large electronic effect on the excess polarizability. The same argument applies to the oligothiophenes up to T5, the experimental results in this case are endcapped by butyl chains connecting the α and β carbon atoms of the thiophene ring.[19]

Another potential source for differences between experimental and calculated results is the environment effect. Experiments are performed in solution or in a solid matrix (or frozen solutions) whereas the calculations correspond to the gas phase. The environment may alter the actual polarizability by intermolecular interactions as it has been shown theoretically[44] but it also complicates the analysis of experimental results from electroabsorption measurements. The change in the excitation energy is related to the local electric field that is felt by the molecule, this field may differ from the externally applied field because of screening by the surrounding solvent. This shielding factor is unknown and is not corrected for in the evaluation of the results.

Triplet B_u excitons

In Table II the excess polarizabilities for states other than the lowest singlet state are also listed for the compounds in Fig. 1. The excess polarizabilities found for the triplet B_u excitons are considerably lower than those found for the singlet excitons. Experimentally, there is very little information on excess polarizabilities of triplet states since these states are not accessible by direct excitation from the ground state. Therefore no triplet data is available from electroabsorption measurements. Long living triplet states can be studied using the FP–TRMC technique if the quantum yield for intersystem crossing is large enough. Triplet polarizabilities have been published only for thiophene oligomers[21] which have an appreciable intersystem crossing yield and the excess polarizabilities were found to be almost an order of magnitude lower than those for singlet excitons which corresponds nicely with the TDDFT calculations presented here. For these triplet polarizabilities there is also a reasonable agreement between the experimental data[21] and calculated results for the shortest oligothiophenes. The polarizabilities for T2 and T3 were calculated to be 3 and 16 Å^3, respectively, whereas the experimental values are 4.5 and 11 Å^3. The experimental results for these triplet states are considerably more reliable than those for the corresponding singlet states because of the very long lifetime of the triplet excited state.

The large difference in excess polarizability between the triplet and singlet exciton can be understood in terms of the sum-over-states description for the polarizability:

$$\alpha_a = \frac{2}{3} \sum_{\substack{n \\ n \neq a}} \frac{|\mu_{na}|^2}{\Delta E_{na}}, \tag{8}$$

where a is the state for which the polarizability is calculated and the sum runs over all states other than a. ΔE_{na} is the

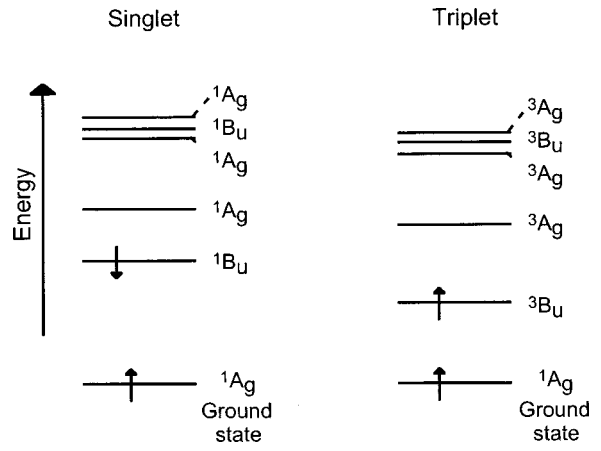

FIG. 4. Schematic energy level diagram and orbital occupation for singlet and triplet states of OPV3.

energy difference between states a and n and μ_{na} is the transition dipole moment between these states. The lowest states for both multiplicities are of B_u symmetry (see Fig. 4 for energy level diagram of OPV3), therefore only excitations to A_g states are allowed. Thus the polarizability of a state of a B_u exciton arises from mixing with A_g states. For the lowest triplet states there are only allowed transitions to higher electronic states and therefore all terms in the summation give a positive contribution to the polarizability. In the case of the lowest singlet exciton the most important contributions are also those resulting from mixing with higher lying A_g states, although there are other contributions that can be considered negligible.[45] The large difference between singlet and triplet excess polarizabilities can be explained by considering the transition energies to the closest lying A_g state. As an example, the calculated energies for the lowest five excitations in OPV3 are listed in Table III for both the triplet and the singlet, and are shown schematically in Fig. 4. The energy difference between the lowest singlet B_u state and the lowest A_g state is 0.24 eV whereas for the triplet this energy difference is 0.79 eV. If it is assumed that the allowed transition with the lowest energy is the main contributor to the polarizability of a certain state it can be understood from Eq. (8) that this contribution will be considerably higher for the singlet exciton than for the triplet if the transition dipole moment is similar. Van der Horst *et al.* have in fact found that in their calculations of exciton polarizabilities of conjugated polymers the main contribution (99%) was due to the mixing with the lowest lying higher state to which a transition was allowed.[25]

TABLE III. Excitation energy (from ground state) for lowest singlet and triplet states in OPV3 in eV.

	Singlet		Triplet	
nr	Energy	Symmetry	Energy	Symmetry
1	2.67	B_u	1.83	B_u
2	2.91	A_g	2.61	A_g
3	3.50	A_g	2.88	A_g
4	3.51	B_u	3.33	B_u
5	3.65	A_g	3.36	A_g

Higher excited states

Table II also lists the excess polarizability of the singlet and triplet A_g exciton states. The ^1A_g column in the table shows some very interesting values. For the longer oligomers of all oligomer series the excess polarizability becomes negative, which implies a decrease in polarizability upon excitation. The decrease in polarizability is of the same order of magnitude as the increases found for the ^1B_u state and are much larger (but negative) than the polarizability for the ground state. A TDDFT calculation of the ground state polarizability of OPV3 for instance gives a value of 61 Å^3. Therefore the lowest ^1A_g states of longer conjugated oligomers are expected to have a negative overall polarizability. This can again be understood by using the same arguments as used above in terms of a sum-over-states description. There is a large negative contribution to the polarizability that arises from the mixing of the ^1A_g state with the ^1B_u state lying below it. This negative contribution is counteracted by positive contributions due to mixing with all higher lying ^1B_u states.

The negative contribution to the excess polarizability for the ^1A_g state is the same as the dominant positive contribution to the polarizability for the ^1B_u state described above. This explains why the absolute values of the ^1B_u and ^1A_g excess polarizabilities are so similar. In the short oligomers a positive value is found for the excess polarizability of the ^1A_g state which shows that the negative contribution is not dominant yet in these cases. Upon lengthening of the chains the energy difference between the B_u and A_g states decreases, which leads to two states that are located in a gap between the ground state and higher lying excited states that are relatively far away in energy. Therefore the response of both states to an applied electric field is dominated by the interaction between them.

Application of an electric field leads to a Stark splitting[46] of the two strongly coupled states in which the energy of the lower state (B_u) decreases quadratically with the applied field, while the energy of the upper state (A_g) increases with the field strength. The lowest (B_u) state attains a dipole moment which has a negative interaction with the applied field (it is directed parallel to the electric field), hence the excitation energy lowers. The upper state shifts to higher energy since it attains a dipole moment which has a positive interaction with the applied field (the direction of this dipole is antiparallel to the electric field). This is an example of the well-known quadratic Stark effect where the upper state formally has a negative polarizability.[46,47]

Similar splitting of states was found theoretically in solvent effect studies of ethylene in its twisted geometry.[48] The electric field of the surrounding solvent induces a splitting between the two lowest excited states and the upper one attains a dipole moment opposite to the electric field and therefore has a negative polarizability.

The quadratic Stark effect has been investigated experimentally by Harrison *et al.* for a ladder-type poly-para-

phenylene using nonlinear optical techniques.[49] It was concluded that the quadratic Stark effect observed for the lowest excited state (B_u) was mainly caused by coupling with the next excited state of A_g symmetry, which is in agreement with the calculations presented here for similar systems and with the earlier results from quasiparticle calculations.[25]

For the triplet A_g state negative polarizabilities might have been expected as well since a negative contribution is present here also due to coupling with the lowest ^3B_u state. However, the energy gap between these two states is considerably larger than in the case of singlet states as shown above (see Table III) and the negative contribution does not become dominant.

SUMMARY AND CONCLUSIONS

This paper describes for the first time a method to calculate electrostatic properties of excited states of molecular systems using time-dependent density functional theory in combination with a static electric field. The method is shown to give reliable results for increases in polarizability upon excitation for short conjugated molecules. For longer conjugated chains an overestimate of the excess polarizability is observed similar to the results found earlier for the ground state. The results for short oligomers are in reasonable agreement with the experimental values from both electroabsorption measurements and time-resolved microwave conductivity measurements (TRMC) for the lowest singlet excited state of B_u symmetry. Triplet polarizabilities for the lowest B_u states are found to be considerably smaller than singlet values, in agreement with experimental observations. The triplet polarizabilities for short thiophene oligomers are found to agree nicely with experimental data for these systems, for the longer chains the polarizability is again considerably overestimated. For the lowest singlet A_g states negative polarizabilities were obtained. The calculated results indicate that the strong coupling between the lowest B_u and A_g states in all oligomers is an important factor which determines the polarizability of both states. The quadratic Stark effect causes a large positive polarizability for the lower state while the higher state (A_g) has a negative polarizability.

This method for the calculation of excited state properties can be a valuable tool in the study of nonlinear optical effects and the nature of electronically excited states in conjugated polymers. The effect of factors such as geometry changes and substituent effects can be studied systematically. This will be the subject of a subsequent paper.

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